

## Supplementary Material

### The efficient *o*-benzenedisulfonimide catalysed synthesis of benzothiazoles, benzoxazoles and benzimidazoles

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## 1. Spectral data of benzothiazoles 9 and benzothiazoline 13c

**2-Phenylbenzothiazole (9a).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  8.04–8.01 (3H, m), 7.88–7.83 (1H, m), 7.48–7.43 (5H, m).<sup>42</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  168.2, 154.3, 135.0, 133.8, 131.1, 129.0, 127.7, 126.5, 125.0, 123.2, 121.5.<sup>42</sup> MS,  $m/z$  (%) = 211 (100) [ $\text{M}^+$ ], 210 (20), 108(15).

**2-(4-Methoxyphenyl)benzothiazole (9b).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  8.02 (2H, d,  $^3J_{\text{HH}}$  8.6 Hz), 7.90 (1H, d,  $^3J_{\text{HH}}$  7.6 Hz), 7.48–7.22 (m, 3H), 6.99 (2H, d,  $^3J_{\text{HH}}$  8.6 Hz), 3.82 (3H, s).<sup>18</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  168.1, 160.5, 154.1, 135.8, 129.9, 126.7, 126.4, 124.5, 122.1, 121.7, 114.0, 55.3.<sup>18</sup> MS,  $m/z$  (%) = 241 (100) [ $\text{M}^+$ ], 226 (35), 198(30).

**2-(4-Chlorophenyl)benzothiazole (9c).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  8.05 (1H, d,  $^3J_{\text{HH}}$  7.6 Hz), 8.00 (2H, d,  $^3J_{\text{HH}}$  8.6 Hz), 7.88 (1H, d,  $^3J_{\text{HH}}$  7.6 Hz), 7.50–7.48 (1H, m, 1H), 7.45 (2H, d,  $^3J_{\text{HH}}$  8.6 Hz), 7.40–7.24 (1H, m).<sup>19</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  166.7, 154.3, 136.9, 134.4, 132.8, 129.9, 128.4, 126.8, 125.2, 123.1, 121.9, 121.7.<sup>19</sup> MS,  $m/z$  (%) = 247 (35), 245 (100) [ $\text{M}^+$ ], 210 (15), 108(20).

**2-(4-Nitrophenyl)benzothiazole (9d).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  8.45–8.38 (1H, m), 8.34 (2H, d,  $^3J_{\text{HH}}$  8.6 Hz), 8.28 (2H, d,  $^3J_{\text{HH}}$  8.6 Hz), 7.99 (1H, d,  $^3J_{\text{HH}}$  7.6 Hz), 7.58–7.45 (2H, m).<sup>20</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  166.9, 154.5, 146.8, 139.3, 134.9, 128.2, 127.0, 126.4, 124.1, 123.8, 121.6.<sup>20</sup> MS,  $m/z$  (%) = 256 (100) [ $\text{M}^+$ ], 210 (35).

**2-Methylbenzothiazole (9e).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  7.90 (1H, dd,  $^3J_{\text{HH}}$  7.4 Hz;  $^4J_{\text{HH}}$  0.8 Hz), 7.75 (1H, td,  $^3J_{\text{HH}}$  7.8 Hz;  $^4J_{\text{HH}}$  1.4 Hz), 7.43–7.24 (2H, m), 2.55 (3H, s).<sup>21</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  166.9, 153.9, 135.8, 125.7, 124.4, 122.1, 121.5, 20.0.<sup>21</sup> MS,  $m/z$  (%) = 149 (100) [ $\text{M}^+$ ], 108 (25).

**2-Benzylbenzothiazole (9f).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  7.94 (1H, d,  $^3J_{\text{HH}}$  8.0 Hz), 7.73 (1H, d,  $^3J_{\text{HH}}$  8.0 Hz), 7.39–7.19 (7H, m), 4.39 (2H, s).<sup>22</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  170.1, 153.5, 137.8, 136.0, 129.8, 129.3, 127.7, 126.2, 125.0, 123.1, 121.8, 40.2.<sup>22</sup> MS,  $m/z$  (%) = 225(80) [ $\text{M}^+$ ], 224 (100), 91(20).

**2-Cyclohexylbenzothiazole (9g).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  7.97 (1H, d,  $^3J_{\text{HH}}$  8.0 Hz), 7.84 (1H, d,  $^3J_{\text{HH}}$  7.6 Hz), 7.38–7.23 (2H, m), 3.12–3.05 (1H, m), 2.18–2.11 (2H, m), 1.86–1.42 (8H, m).<sup>23</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  174.4, 152.5, 133.2, 124.4, 123.7, 121.2, 120.4, 42.4, 32.1, 25.8, 25.0.<sup>23</sup>

MS,  $m/z$  (%) = 217 (20) [ $\text{M}^+$ ], 188 (25), 162 (100), 149 (75).

**2-*t*-Butylbenzothiazole (9h).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  7.81 (1H, d,  $^3J_{\text{HH}}$  8.0 Hz), 7.77 (1H, d,  $^3J_{\text{HH}}$  8.0 Hz), 7.38–7.21 (2H, m), 1.46 (9H, s).<sup>24</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  179.2, 153.5, 134.8, 125.4, 124.0, 122.2, 121.5, 38.6, 30.8.<sup>24</sup> MS,  $m/z$  (%) = 191 (20) [ $\text{M}^+$ ], 176 (100).

**5-Chloro-2-phenylbenzothiazole (9i).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  8.10–8.06 (3H), 7.75 (1H, d,  $^3J_{\text{HH}}$  8.4 Hz), 7.58–7.45 (3H, m), 7.31 (1H, d,  $^3J_{\text{HH}}$  8.4 Hz).<sup>25</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  169.8, 155.5, 133.3, 132.0, 130.9, 128.8, 127.7, 125.6, 123.4, 122.1.<sup>25</sup> MS,  $m/z$  (%) = 247 (30), 245 (100) [ $\text{M}^+$ ].

**5-Chloro-2-methylbenzothiazole (9j).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  7.85 (1H, s), 7.68 (1H, d,  $^3J_{\text{HH}}$  8.4 Hz), 7.21 (1H, d,  $^3J_{\text{HH}}$  8.4 Hz), 2.75 (3H, s).<sup>26</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  169.0, 154.3, 133.4, 131.0, 125.9, 122.5, 121.7, 19.9.<sup>43</sup> MS,  $m/z$  (%) = 185 (30), 183 (100) [ $\text{M}^+$ ], 149 (35), 116(25).

**2-(2-Methoxyphenyl)benzothiazole (9k).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  8.52 (1H, d,  $^3J_{\text{HH}}$  7.6 Hz), 8.08 (1H, d,  $^3J_{\text{HH}}$  7.6 Hz), 7.85 (1H, d,  $^3J_{\text{HH}}$  7.6 Hz) 7.47–6.99 (5H, m), 4.00 (3H, s). $^{27}$   $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  167.0, 157.5, 154.8, 136.1, 129.9, 128.7, 126.0, 125.6, 122.4, 121.9, 121.8, 121.4, 113.7, 55.8. $^{27}$  MS,  $m/z$  (%) = 241 (100) [ $\text{M}^+$ ], 240 (35), 212(45), 136(55).

**2-(3-Methoxyphenyl)benzothiazole (9l).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  8.04 (1H, d,  $^3J_{\text{HH}}$  8.0 Hz), 7.88 (1H, d,  $^3J_{\text{HH}}$  7.6 Hz), 7.67–7.52 (2H, m), 7.48–7.30 (3H, m), 7.18–7.00 (1H, m), 3.87 (3H, s). $^{19}$   $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  167.9, 158.4, 154.1, 135.1, 133.8, 129.9, 126.6, 125.8, 123.4, 121.3, 120.8, 117.9, 113.1, 55.2. $^{19}$  MS,  $m/z$  (%) = 241 (100) [ $\text{M}^+$ ], 240 (75), 212(35), 211(45).

**2-(2-Indolyl)benzothiazole (9m).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  8.72 (1H, br s), 8.01 (1H,  $^3J_{\text{HH}}$  d, 8.4 Hz), 7.89 (1H, d,  $^3J_{\text{HH}}$  7.6 Hz), 7.74 (1H, d,  $^3J_{\text{HH}}$  8.4 Hz), 7.50–7.15 (7H, m). $^{28}$   $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  166.8, 154.0, 137.0, 134.9, 128.4, 127.1, 125.4, 124.9, 123.0, 121.6, 121.4, 120.8, 111.4, 106.0. $^{28}$  MS,  $m/z$  (%) = 250 (100) [ $\text{M}^+$ ].

**2,2-Dimethylbenzothiazoline (13c).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  7.02–6.82 (2H, m), 6.72–6.61 (2H, m), 1.67 (6H, s). $^{29}$   $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ )  $\delta_{\text{C}}$  145.7, 128.4, 124.9, 121.7, 111.5, 75.2, 30.8. MS,  $m/z$  (%) = 165 (20) [ $\text{M}^+$ ], 150(100), 109(25).

## 2. Spectral data of benzoxazoles 10 and benzoxazoline 20b

**Phenylbenzoxazole (10a).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  8.21–8.18 (2H, m), 7.69–7.61 (2H, m), 7.59–7.53 (3H, m), 7.38–7.33 (2H, m). $^{30}$   $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  163.2, 151.9, 142.4, 131.1, 128.8, 127.5, 127.2, 125.5, 124.6, 120.7, 110.8. $^{30}$  MS,  $m/z$  (%) = 195 (100), [ $\text{M}^+$ ], 167 (15), 63 (20).

**2-(2-Methoxyphenyl)benzoxazole (10b).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  8.18–8.14 (1H, m), 7.89–7.80 (1H, m), 7.68–7.50 (2H, m) 7.44–7.39 (2H, m), 7.19–7.10 (2H, m), 4.04 (3H, s). $^{31}$   $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  161.2, 158.5, 150.8, 142.1, 132.9, 131.5, 124.9, 124.0, 120.5, 120.2, 116.8, 112.7, 110.5, 56.4. $^{31}$  MS,  $m/z$  (%) = 225 (100) [ $\text{M}^+$ ], 196 (55).

**2-(3-Methoxyphenyl)benzoxazole (10c).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  7.88 (1H, d,  $^3J_{\text{HH}}$  8.6 Hz), 7.77–7.75 (2H, m), 7.57–7.52 (1H, m), 7.47–7.41 (1H, m), 7.37–7.34 (2H, m), 7.10–7.05 (1H, m), 3.91 (3H, s). $^{31}$   $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  162.9, 159.3, 150.7, 141.6, 129.8, 128.7, 125.3, 124.1, 119.9, 119.7, 118.0, 111.5, 110.7, 55.2. $^{31}$  MS,  $m/z$  (%) = 225 (100) [ $\text{M}^+$ ], 196 (25).

**2-(4-Methoxyphenyl)benzoxazole (10d).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  8.24 (2H, d,  $^3J_{\text{HH}}$  8.6 Hz), 7.78–7.74 (1H, m), 7.59–7.55 (2H, m), 7.00 (2H, d,  $^3J_{\text{HH}}$  8.6 Hz), 3.91 (3H, s). $^{32}$   $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  166.0, 162.5, 150.4, 142.9, 129.5, 124.7, 124.3, 120.0, 119.4, 115.0, 111.3, 55.3. $^{32}$  MS,  $m/z$  (%) = 225 (100) [ $\text{M}^+$ ], 210 (15), 182(44), 63(70).

**2-(4-Chlorophenyl)benzoxazole (10e).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  8.15 (2H, d,  $^3J_{\text{HH}}$  8.6 Hz), 7.78–7.76 (1H, m), 7.54–7.50 (1H, m), 7.47 (2H, d,  $^3J_{\text{HH}}$  8.6 Hz), 7.34–7.31 (2H, m). $^{32}$   $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  162.4, 150.9, 142.1, 137.9, 129.6, 128.4, 125.5, 125.1, 124.9, 120.4, 110.9. $^{32}$  MS,  $m/z$  (%) = 231 (35), 229 (100) [ $\text{M}^+$ ], 166 (25), 192(15), 63(80).

**2-(4-Nitrophenyl)benzoxazole (10f).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  8.41 (2H, d,  $^3J_{\text{HH}}$  9.0 Hz), 8.33 (2H, d,  $^3J_{\text{HH}}$  9.0 Hz), 7.80–7.77 (1H, m), 7.61–7.55 (1H, m), 7.42–7.37 (2H, m). $^{32}$   $^{13}\text{C}$

NMR (50 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{C}}$  160.9, 151.5, 149.0, 142.1, 132.4, 128.1, 126.9, 125.5, 124.1, 120.9, 111.1.<sup>32</sup> MS,  $m/z$  (%) = 240 (100) [M<sup>+</sup>], 210 (45), 63(85).

**2-Methylbenzoxazole (10g).** <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{H}}$  7.61–7.57 (1H, m), 7.43–7.39 (1H, m), 7.27–7.20 (2H, m), 2.58 (3H, s).<sup>33</sup> <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{C}}$  163.9, 150.5, 142.1, 125.0, 124.3, 119.9, 110.7, 15.1.<sup>33</sup> MS,  $m/z$  (%) = 133 (100) [M<sup>+</sup>], 104 (15), 63 (15).

**2-Benzylbenzoxazole (10h).** <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{H}}$  7.74–7.71 (1H, m), 7.49–7.43 (1H, m), 7.35–7.21 (7H, m), 4.20 (2H, s).<sup>31</sup>

<sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{C}}$  164.1, 150.7, 141.6, 134.9, 128.9, 128.6, 127.0, 124.4, 123.8, 119.5, 110.1, 35.7.<sup>31</sup> MS,  $m/z$  (%) = 209(100) [M<sup>+</sup>], 180 (25), 91(45).

**6-Methyl-2-phenylbenzoxazole (10i).** <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{H}}$  8.28–8.21 (2H, m), 7.60 (1H, d, <sup>3</sup>J<sub>HH</sub> 8.6 Hz), 7.55–7.50 (3H, m), 7.32 (1H, s), 7.11 (1H, d, <sup>3</sup>J<sub>HH</sub> 8.0 Hz), 2.47 (3H, s).<sup>33</sup> <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{C}}$  162.9, 151.4, 139.7, 135.9, 131.4, 128.7, 127.2, 127.1, 125.9, 119.9, 111.1, 21.4.<sup>33</sup>

MS,  $m/z$  (%) = 209 (100) [M<sup>+</sup>], 180 (15), 78(15).

**2,6-Dimethylbenzoxazole (10j).** <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{H}}$  7.55 (1H, d, <sup>3</sup>J<sub>HH</sub> 8.6 Hz), 7.29 (1H, s), 7.13 (1H, d, <sup>3</sup>J<sub>HH</sub> 8.6 Hz), 2.68 (3H, s), 2.52 (3H, s).<sup>33</sup> <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{C}}$  163.9, 151.5, 140.0, 134.9, 124.8, 118.9, 110.7, 21.2, 15.1.<sup>33</sup> MS,  $m/z$  (%) = 147 (100) [M<sup>+</sup>], 106 (35), 78(55).

**6-Nitro-2-phenylbenzoxazole (10k).** <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{H}}$  8.55 (1H, s), 8.40–8.32 (3H, m), 7.81 (1H, d, <sup>3</sup>J<sub>HH</sub> 8.6 Hz), 7.51–7.35 (3H, m).<sup>34</sup> <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{C}}$  163.5, 151.0, 148.0, 144.9, 129.5, 128.7, 127.9, 126.7, 120.1, 119.8, 106.8.<sup>34</sup> MS,  $m/z$  (%) = 240 (100) [M<sup>+</sup>], 210 (15).

**2-Methyl-6-nitrobenzoxazole (10l).** <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{H}}$  8.42 (1H, s), 8.22–8.19 (1H, m), 7.74 (1H, d, <sup>3</sup>J<sub>HH</sub> 8.6 Hz), 2.61 (3H, s).<sup>34</sup> <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{C}}$  166.3, 151.3, 148.6, 144.4, 120.6, 119.7, 107.1, 14.5.<sup>44</sup> MS,  $m/z$  (%) = 178 (100) [M<sup>+</sup>], 148(25).

**2,2-Dimethylbenzoxazoline (20b).** <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{H}}$  6.74–6.62 (4H, m), 1.89 (6H, s).<sup>35</sup> <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{C}}$  141.9, 130.8, 121.7, 117.9, 116.0, 114.9, 79.0, 30.2.<sup>35</sup> MS,  $m/z$  (%) = 149 (25) [M<sup>+</sup>], 134(100).

### 3. Spectral data of benzimidazoles 11

**2-Phenylbenzimidazole (11a).** <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{H}}$  12.5 (1H, br s), 8.03–8.00 (2H, m), 7.67–7.51 (2H, m), 7.31–7.29 (3H, m), 7.19–7.12 (2H, m).<sup>36</sup> <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{C}}$  151.9, 144.1, 135.5, 130.8, 129.9, 128.2, 126.0, 122.9, 121.0, 118.7, 111.2.<sup>36</sup> MS,  $m/z$  (%) = 194 (100), [M<sup>+</sup>], 193 (25).

**2-(4-Methoxyphenyl)benzimidazole (11b).** <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{H}}$  12.45 (1H, br s), 8.18–8.11 (2H, m), 7.68–7.64 (2H, m), 7.17–6.99 (4H, m), 3.90 (3H, s).<sup>36</sup> <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{C}}$  160.9, 153.3, 137.4, 128.8, 123.1, 115.0, 114.8, 55.0. MS,  $m/z$  (%) = 224 (100) [M<sup>+</sup>], 223 (35), 182(44), 69(100).<sup>36</sup>

**2-(4-Chlorophenyl)benzimidazole (11c).** <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{H}}$  12.65 (1H, br s), 8.15 (2H, d, <sup>3</sup>J<sub>HH</sub> 8.6 Hz), 7.68–7.49 (4H, m), 7.24–7.21 (2H, m).<sup>37</sup> <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>COCD<sub>3</sub>):  $\delta_{\text{C}}$  153.4, 139.2, 129.9, 128.7, 122.5, 122.0, 118.6, 111.2.<sup>37</sup> MS,  $m/z$  (%) = 230 (35), 228 (100) [M<sup>+</sup>], 149 (35), 57(100).

**2-(4-Nitrophenyl)benzimidazole (11d).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  12.98 (1H, br s), 8.05–8.00 (2H, m), 7.88–7.75 (2H, m), 7.59–7.54 (2H, m), 7.25–7.21 (2H, m).<sup>36</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  151.9, 148.5, 144.6, 136.7, 135.6, 131.2, 125.6, 124.2, 122.1, 120.1, 113.9.<sup>36</sup> MS,  $m/z$  (%) = 239 (100) [ $\text{M}^+$ ], 209 (15), 57 (100).

**2-Methylbenzimidazole (11e).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  12.45 (1H, br s), 7.60–7.54 (2H, m), 7.43–7.39 (1H, m), 7.22–7.19 (2H, m), 2.64 (3H, s).<sup>38</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  152.9, 136.9, 128.9, 128.5, 126.7, 121.9, 35.1.<sup>38</sup> MS,  $m/z$  (%) = 132 (100) [ $\text{M}^+$ ], 131 (75).

**2-Benzylbenzimidazole (11f).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  12.12 (1H, br s), 7.48 (2H, m), 7.37–7.33 (5H, m), 7.21–7.10 (2H, m), 4.22 (2H, s).<sup>39</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  153.4, 138.9, 136.2, 129.1, 128.7, 128.4, 126.4, 121.2, 115.6, 34.9.<sup>39</sup> MS,  $m/z$  (%) = 208(100) [ $\text{M}^+$ ], 207 (55), 91(25).

**2-Cyclohexylbenzimidazole (11g).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  12.16 (1H, br s), 7.55–7.51 (2H, m), 7.27–7.23 (2H, m), 2.85–2.75 (1H, m), 2.20–2.14 (2H, m), 1.90–1.25 (8H, m).<sup>25</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  155.9, 144.1, 135.7, 122.9, 121.0, 118.9, 112.7, 38.9, 31.6, 25.9, 25.6.<sup>25</sup> MS,  $m/z$  (%) = 208(100) [ $\text{M}^+$ ], 207 (55), 91(25).

**2-*t*-Butylbenzimidazole (11h).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  12.00 (1H, br s), 7.50–7.48 (2H, m), 7.16–7.05 (2H, m), 1.31 (3H, s).<sup>36</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  156.7, 143.8, 134.9, 123.4, 120.5, 118.8, 111.4, 33.2, 29.3.<sup>36</sup> MS,  $m/z$  (%) = 174(100) [ $\text{M}^+$ ], 173 (65).

**5-Methyl-2-phenylbenzimidazole (11i).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  12.77 (1H, br s), 8.29–8.21 (2H, m), 7.55–7.38 (5H, m), 7.00–6.94 (1H, m), 2.48 (3H, s).<sup>40</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  152.2, 138.1, 134.7, 131.3, 130.0, 129.7, 128.8, 127.5, 125.1, 114.6, 114.0, 24.0.<sup>40</sup> MS,  $m/z$  (%) = 208(100) [ $\text{M}^+$ ].

**2,5-Dimethylbenzimidazole (11j).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  12.15 (1H, br s), 7.42 (1H, d,  $^3J_{\text{HH}}$  7.6 Hz), 7.24 (1H, s), 6.99 (1H, d,  $^3J_{\text{HH}}$  7.6 Hz), 2.47 (3H, s), 2.38 (3H, s).<sup>41</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  152.2, 138.2, 135.4, 132.0, 124.9, 114.3, 114.1, 24.1, 16.8.<sup>41</sup> MS,  $m/z$  (%) = 146(100) [ $\text{M}^+$ ].

**5-Nitro-2-phenylbenzimidazole (11k).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  13.00 (1H, br s), 8.55–8.47 (1H, m), 8.25–8.18 (1H, m), 8.13–8.09 (2H, m), 7.55–7.47 (4H, m).<sup>40</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  149.9, 143.7, 142.6, 139.4, 130.9, 129.1, 129.0, 127.7, 118.5, 116.5, 111.9.<sup>40</sup> MS,  $m/z$  (%) = 239 (100) [ $\text{M}^+$ ].

**5-Nitro-2-methylbenzimidazole (11l).**  $^1\text{H}$  NMR (200 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{H}}$  12.77 (1H, br s), 8.29 (1H, s), 8.07–8.05 (2H, m), 7.69–7.65 (2H, m), 2.55 (3H, s).<sup>38</sup>  $^{13}\text{C}$  NMR (50 MHz,  $\text{CD}_3\text{COCD}_3$ ):  $\delta_{\text{C}}$  153.5, 146.4, 143.0, 139.7, 117.5, 116.6, 111.0, 16.4.<sup>38</sup> MS,  $m/z$  (%) = 177(100) [ $\text{M}^+$ ].

## 4. References

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